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# Thermal Decomposition of Cobalt-free $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ Cathode for Intermediate Temperature Solid Oxide Fuel Cell

Nurul Akidah Baharuddin[a], Andanastuti Muchtar[a,b*], Mahendra Rao Somalu[a], Abdullah Abdul Samat[a]

[a]*Fuel Cell Institute,Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*

[b]*Department of Mechanical & Materials Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia*

**Abstract**

$SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ (SFT) was synthesized through glycine-nitrate combustion to elucidate its thermal decomposition behavior. In this work, dark precursor powders were obtained after combustion was completed. Thermogravimetric analysis (TGA) was conducted at room temperature to 1200 °C in static air with a heating rate of 10 °Cmin$^{-1}$ for the as-prepared precursor powders. The total weight loss of 10.59 % was obtained at temperature 1060 °C. The decomposition mechanism of perovskite oxide SFT was observed through Fourier transform infrared spectroscopy. X-ray diffraction (XRD) analysis confirmed the formation of cobalt-free SFT cathode with appearance of secondary phase $Sr_3Fe_2O_6$ at 1100 °C. These results provide useful information to propose the calcination temperature of the synthesized powders.


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*Keywords:* Thermal decomposition; Glycine-nitrate combustion; Calcination

## 1. Introduction

Intermediate-temperature solid oxide fuel cells (ITSOFC) have been fabricated using newly developed materials for each component (anode, electrolyte and cathode) in order to reduce the operating temperatures below 800 ºC. For

* Corresponding author. Tel.: +60389213895; fax: +60389118314.
*E-mail address:* muchtar@ukm.edu.my


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cathode, many materials including cobalt-free perovskite-based have been introduced [1]. The presence of cobalt causes an increase in electro catalytic activity in oxygen reduction [2,3]. Nevertheless, cobalt-containing cathode increases the thermal expansion coefficient of materials and consequently reduce the cell electrochemical performance due to thermal mismatch with electrolytes [4-7].

A cobalt-free $SrFe_{1-x}Ti_xO_{3-\delta}$ cathode has been produced via a solid state reaction [7,8]. However, the formation of $SrFe_{1-x}Ti_xO_{3-\delta}$ cathode powder through wet techniques has yet to be investigated. In our work, cobalt-free $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ cathode was produced via a wet technique called glycine-nitrate combustion (GNC). $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ cathode powders were prepared and their thermal decomposition behavior was examined to understand cathode powder formation.

## 2. Experimental

### *2.1. Powder preparation*

This work focused on $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ cathode powders formation via GNC method. Glycine ($NH_2CH_2COOH$) together with metal nitrate; strontium nitrate, $Sr(NO_3)_2$ and iron nitrate, $Fe(NO_3)_3.9H_2O$ and titanium butoxide, $Ti(C_4H_9O)_4$ were utilized as raw materials (Sigma Aldrich). The Stoichiometric amounts of raw materials were used. Titanium butoxide mentioned earlier was used to prepare titanyl nitrate through hydrolysis (1) and nitration (2).

Hydrolysis:

$$Ti(C_4H_9O)_4+3H_2O\rightarrow TiO(OH)_2+4C_4H_9OH \quad (1)$$

Nitration:

$$TiO(OH)_2+2HNO3\rightarrow TiO(NO_3)_2+2\ H_2O \quad (2)$$

The nitrates were stirred until a homogeneous nitrate solution was obtained. Glycine was added to the solution at a stoichiometric ratio to nitrates (0.55). The glycine/nitrates (G/N) ratio was calculated in accordance with propellant chemistry principle [9,10]. General glycine-nitrate combustion reaction as in equation (3):

$$Sr(NO_3)_2+0.9Fe(NO_3)_3.9H_2O+0.1TiO(NO_3)_2+xNH_2CH_2COOH\rightarrow SrFe0.9Ti0.1\ O_{3-\delta}+AN_2+BCO_2+CH_2O \quad (3)$$

According to propellant chemistry principle, the oxidizing valence is -24.5, the elemental stoichiometric coefficient ($Ø_e$) is 2.7 and the total nitrate molecule is 4.9. Thus, the stoichiometric G/N is 2.7/4.9 or 0.55. Hence *x, A, B* and *C* were calculated. Equation (4) is derived:

$$Sr(NO_3)_2+0.9Fe(NO_3)_3.9H_2O+0.1TiO(NO_3)_2+2.7NH_2CH_2COOH\rightarrow SrFe0.9Ti0.1\ O_{3-\delta}+3.8N_2+5.4CO_2+6.8H_2O \quad (4)$$

The solution was continuously stirred for 1h; afterward, the temperature was increased to 350 °C to form a dark precursor $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ powders. The precursor powders were then subjected to thermal decomposition analysis.

### *2.2. Thermal decomposition analysis*

The thermal decomposition behavior of the synthesized powders was analyzed through TGA by using a Pyris Diamond TG/DTG analyzer. TGA was conducted in static air from 30 ºC – 1200 ºC at a heating rate of 10 ºCmin$^{-1}$. A TG curve was examined and the decomposition temperature of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ was proposed.

### *2.3. SrFe0.9Ti0.1O3-δ formation analysis*

On the basis of the TGA result, we calcined the precursor powders at the proposed temperature for 5h. The formation of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ related to calcination was evaluated using a PerkinElmer FTIR spectrometer. The phase structure of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ was confirmed through XRD analysis.

## 3. Result and Discussion

GNC occurred with several flame types, such as smouldering, flaming or explosive. Fig. 1. shows the combustion process for $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ powders formation from the initial (step 1) until the end of combustion (step 6). The flame type depends on the fuel-to-nitrate ratio and the fuel type [11]. The flaming type of flame was observed in this work during combustion because of the selected stoichiometric G/N ratio (0.55). The excess amount of the G/N ratio can cause the formation of explosive flames; by contrast insufficient fuel can produce smouldering flame. Combustion was completed in 90 s.


Fig. 1. Combustion (step 1 – 6) of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ powders.

Fig.2. illustrates the TG-DTG curves of the precursor $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ powders. The TG curve revealed three main regions where weight losses were observed. From the initial temperature to 370 ºC, 0.68 % of weight loss was found due to elimination of water [12]. In the second stage, 1.08 % of weight loss was detected from 475 ºC to 550 ºC because of the decomposition of nitrates and carbon [6]. In the final stage, 8.83 % of weight loss was noted from 700 ºC to 1060 ºC due to the degradation of carbon residue and the formation of desired oxides [12]. The total weight loss of 10.59 % was obtained before the oxide was formed. Hence, the calcination was proposed at temperature above 1060 ºC. The DTG curve confirmed the weight losses through the appearance of downward peak in all of the three stages at the given temperature range.

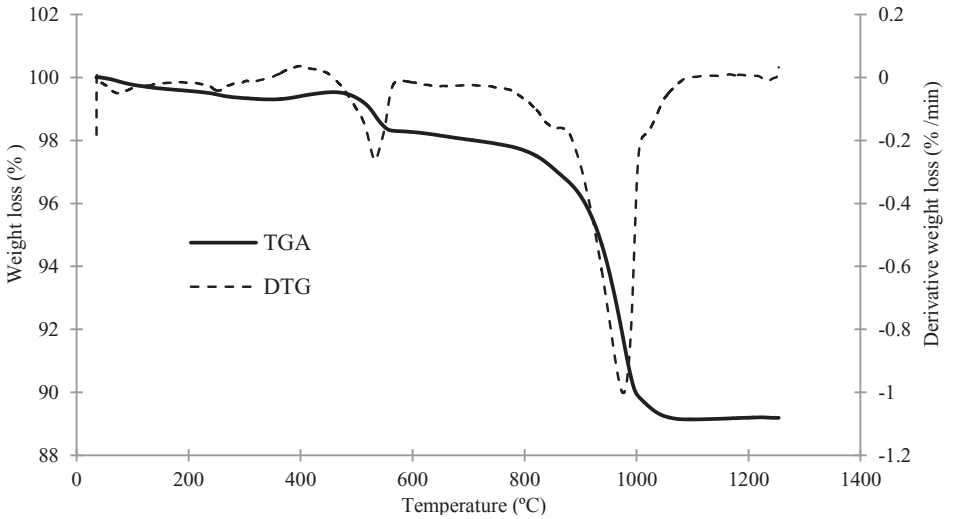


Fig. 2. TG-DTG curves of the decomposition of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ heated at 30 ºC to 1200 ºC.

The TG-DTG curves were extensively interpreted through FTIR analysis. Fig. 3. shows the IR spectra of the precursor and calcined powders. Graph I represents the IR spectra of the precursor powders; graph II and III illustrate the IR spectra of the powders calcined at 700 and 1100 ºC, respectively. The peaks of the precursor powders (I) appeared at 570 – 600, 860, 1400 – 1600 and 3500 $cm^{-1}$. At 3500 $cm^{-1}$, the peak is attributed to the stretching mode of the bound water molecule. At 1400 – 1600 $cm^{-1}$, the O-H functional group appears because of in-plane bending. This peak broadens when the powders were calcined at 700 and 1100 ºC due to the elimination of water or humidity from the sample. A sharp peak is found at approximately 1400 $cm^{-1}$ and thus confirms the presence of nitrates in the precursor powders. This peak disappeared when powders were calcined at 700 ºC (II) and 1100 ºC (III). The peak at 860 $cm^{-1}$ corresponds to the carbonate functional group C(=O)(O–)2. The intensity of the peak was reduced when the powders were calcined at 700 ºC (II). This carbonate functional group completely disappeared when the powders were calcined at 1100 ºC (III) due to the carbon decomposition. The peak at 570 – 600 cm-1 is attributed to the desired oxide [13]. This peak is detected in the three graph; it also became sharp as the powder was calcined to 1100 ºC. Therefore, cobalt-free $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ cathode powders were formed. The purity of the $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ was analyzed through XRD.

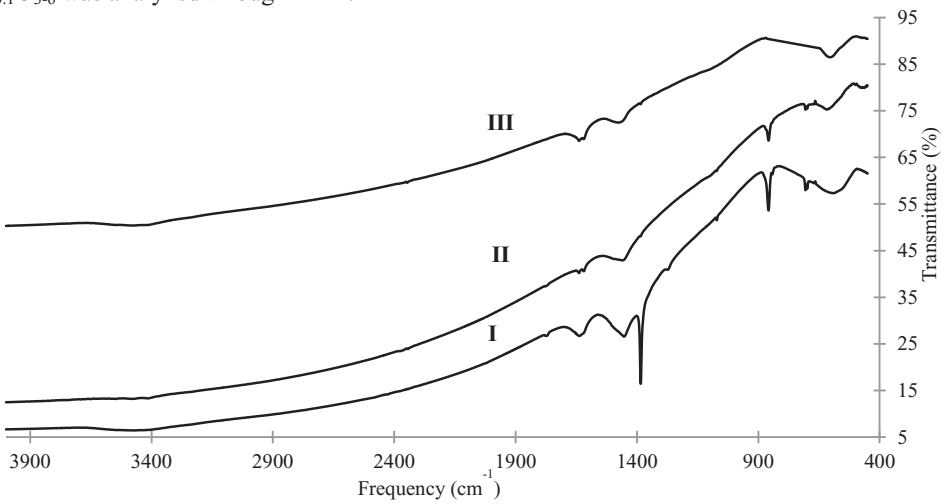


Fig. 3. IR spectra of uncalcined $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ powders (I); IR spectra of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ powders calcined at 700 °C (II) and at 1100 °C (III).

Fig. 4. shows the XRD pattern of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ calcined at 1100 ºC for 5h. The XRD pattern indicates that a cubic perovskite (pm-3m) of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ was formed after calcination was completed. Yang at al. (2015) produced powders with the same composition but used a different technique, namely, sol-gel; they also found that a cubic pm-3m structure is formed [14]. Unfortunately, in this study, the secondary phase of $Sr_3Fe_2O_6$ was also obtained. The peaks of the secondary phase exist at 2θ = 33° in the following ranges: 40°–50°, 50°–60°, and around 68°. The secondary phase formation can be caused by insufficient heat (temperature) and short holding time [15]. Increasing the calcination temperature with sufficient holding time leads to the decomposition of the undesired phase. The amount of temperature increase must be selected carefully because of the grain growth effect. As grains grow, particle size increases, and the surface area for oxygen reduction decreases [16,17]. This phenomenon determines the electrochemical performance of cathodes. Calcination in a pellet form has also been proposed to obtain high-purity single-phase oxides [18]. Thus, calcination should be performed in a pellet form at higher temperatures and longer holding times in further studies to produce high-purity cobalt-free $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ cathode.

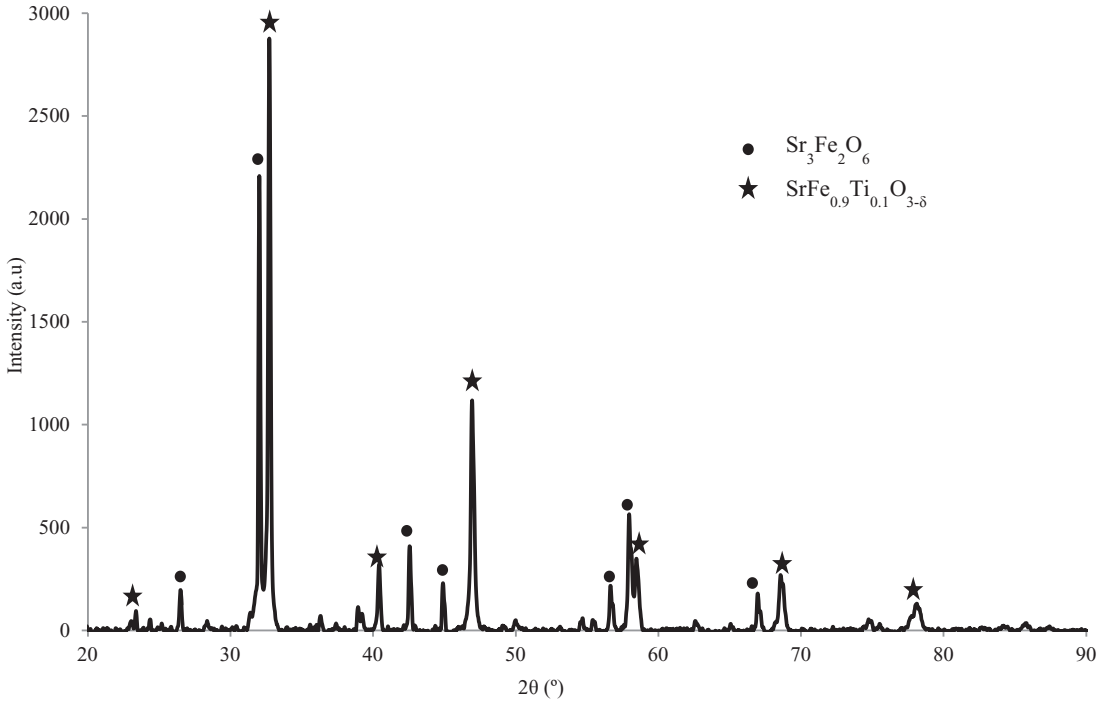


Fig. 4. XRD pattern for $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ with presence of secondary phase $Sr_3Fe_2O_6$.

## 4. Conclusions

Cobalt-free $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ cathode was successfully prepared via GNC method. Flaming type of flame was observed throughout the combustion process. The precursor powders of $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$ were subjected to thermal decomposition analysis through TGA and FTIR analysis. A total weight loss of 10.59% was obtained through TGA. The desired oxide was formed at approximately 1060 °C. Thus, calcination was conducted at 1100 °C for 5 h. The XRD pattern confirmed the formation of cubic perovskite SrFe0.9Ti0.1O3-δ and the existence of the undesired peaks of the secondary oxide phase, namely, $Sr_3Fe_2O_6$. As a result, calcination at temperatures higher than 1100 °C and in a pellet form should be further investigated to eliminate the secondary oxide phase and to produce high-purity $SrFe_{0.9}Ti_{0.1}O_{3-\delta}$.

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